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Constituents of the Essential Oil of *Chrysanthemum japonense*. Nojigiku Alcohol and Its Acetate

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The essential oil of *Chrysanthemum japonense* has been analyzed to isolate a new monoterpenoid named nojigiku alcohol together with its acetate, the structure of which has been elucidated as (5*R*)-2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptan-5-ol. In addition, fifteen monoterpenoids including (+)-α-pinene, (+)-camphene, β-pinene, sabinene, 1,8-cineole, *p*-cymene, filifolone, (+)-chrysanthenone, (+)-camphor, (+)-borneol, (−)-*cis*- and (+)-*trans*-chrysanthenyl acetate, *cis*- and *trans*-carveyl acetate, (+)-bornyl acetate and nine sesquiterpenoids including α-copaene, β-elemene, β-caryophyllene, germacrene-D, γ-cadinene, calamenene, β-caryophyllene oxide, T-muurolol and α-cadinol were identified in the essential oil.

In Japan about twenty species of the *Genus Chrysanthemum* (the *family* of *Compositae*) are distributed as native plants. The plants are known to be a typical group, the chromosome number of which are the multiple such as $2n=18$, 36, 54, 72, and 90.[1)] Consequently, they have been investigated by many workers in the field of the botany, especially taxonomy, morphology, cytology and genetics. However, there has been little chemical investigation on the constituents of the essential oils except for the isolation of chrysanthenone from *Chrysanthemum sinense* Sabin, (an agricultural species) and its structural elucidation by Kotake and Nonaka.[2)]

The present author is continuing the investigation on the essential oils of the species, and has already reported the structural elucidations of (+)-*trans*-chrysanthenyl acetate,[3)] two new acetylenic compounds,[4)] and also the analyses of the essential oils of *Ch. boreale* Makino ($2n=18$),[5)] *Ch. makinoi* Matsum. *et* Nakai ($2n=18$),[5)] *Ch. shiwogiku* Kitam. ($2n=54$)[3)] and *Ch. japonense* var. *devile* Kitam. ($2n=54$).[6)] In the present work, the essential oil of *Ch. japonense* (Makino) Nakai ($2n=54$) has been analyzed and a new monoterpene alcohol isolated of good aroma, (5*R*)-2,2-dimethyl-3-methylenebicyclo[2.2.1]heptan-5-ol (**1**), together with its acetate (**2**). The alcohol has been named nojigiku alcohol and its structure elucidated as 5-hydroxycamphene. This is the first example of an oxygenated derivative of camphene having been isolated in nature. The details of the structural elucidation and the analytical results on other mono and sesquiterpenoids are described. Part of the work has been presented in a prelininary report.[7)]

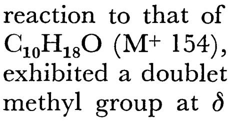
Results and Discussion

Structural Elucidation of Nojigiku Alcohol and Its Acetate. Nojigiku alcohol (**1**), mp 52.0—53.0 °C, $[\alpha]_D^{25}$ +12.0° (*c* 1.10, $CHCl_3$), has been isolated, together with an oily acetate, $[\alpha]_D^{25}$ +20.9° (*c* 0.58, $CHCl_3$) from the essential oil by a combination of fractional distillation and elution chromatography.

The alcohol has been analyzed for $C_{10}H_{16}O$ (M^+ 152) and afforded a crystalline 3,5-dinitrobenzoate, mp 107.0—108.0 °C. The IR and ^1H-NMR spectra revealed the alcohol to contain a secondary hydroxyl group (δ 3.71, 1H, dd, $J=7.0$ and 3.0 Hz; ν 3350 and 1050 cm^{-1}), a *gem*-dimethyl (δ 0.91 and 1.01, each 3H, s; ν 1380, 1375, and 1360 cm^{-1}), an allylic methine (δ 2.63, 1H, br s), and an *exo*-methylene group (δ 4.60 and 4.81, each 1H, s; ν 3060, 1655, and 885 cm^{-1}).

Examination of the ^{13}C-NMR spectrum showed a close resemblance to that of camphene, which is a bicyclic monoterpene hydrocarbon containing all the functional groups mentioned above except the secondary hydroxyl group. The chemical shifts and the signal multiplicities are shown in Table 1. In the catalytic hydrogenation over Adams catalyst in AcOH, the alcohol took up one molar equivalent of hydrogen to afford two saturated alcohols attributable to the *endo*- and *exo*-methyl isomers in a ratio of 4: 1, a similar reaction to that of camphene; the major product (**4**), $C_{10}H_{18}O$ (M^+ 154), after isolation by preparative GLC, exhibited a doublet due to the newly formed secondary methyl group at δ 0.90. These results suggested the alcohol to be a bicyclic monoterpene alcohol. The alcohol was oxidized with Jones reagent to give a nonconjugated cyclopentanone derivative (**3**), $C_{10}H_{14}O$ (M^+ 150.1049); mp 47.0—48.0 °C (semicarbazone, mp 189.0—190.0 °C); ν 1755 cm^{-1}, leaving the *exo*-methylene group unaffected (δ 4.82 and 5.06, each 1H, s; ν 3075, 1655, and 899 cm^{-1}). In the spectra of this ketone, an absorption band attributable to the newly formed active methylene appeared at ν 1420 cm^{-1} and the broad singlet of the allylic methine showed a much lower shift (δ 3.00) owing to the anisotropic effect of the carbonyl group compared with the original alcohol. Thus, nojigiku alcohol was characterized as a camphene derivative bearing the hydroxyl group on the C-5 position, that is, the planar structure of nojigiku alcohol was determined as 2,2-dimethyl-3-methylenebicyclo-[2.2.1]heptan-5-ol.

On treatment with acetic anhydride in pyridine, the



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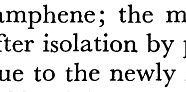

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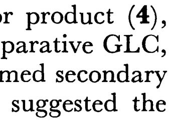

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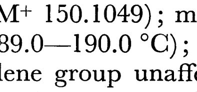

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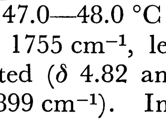

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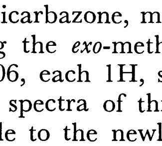

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TABLE 1. ^{13}C-NMR SPECTRAL DATA$^{a)}$ OF NOJIGIKU ALCOHOL (**1**), ITS ACETATE (**2**) AND CAMPHENE (**7**), AND SHIELDING DIFFERENCES

Carbon atom	**1**	**2**$^{b)}$	**7**$^{c)}$	$\Delta\delta$(**1**—**7**)$^{d)}$	$\Delta\delta$(**2**—**7**)$^{d)}$
1	48.4(d)	47.5(d)	48.8(d)	−0.4(γ)	−1.3(γ)
2	41.5(s)	41.2(s)	42.3(s)	−0.8(δ)	−1.1(δ)
3	163.2(s)	159.7(s)	167.9(s)	−4.7(γ)	−8.2(γ)
4	56.4(d)	52.5(d)	47.6(d)	8.8(β)	4.9(β)
5	74.4(d)	76.3(d)	29.2(t)	45.2(α)	47.1(α)
6	36.9(t)	34.2(t)	24.1(t)	12.8(β)	10.1(β)
7	33.9(t)	34.2(t)	37.9(t)	−4.0(γ)	−3.7(γ)
8	104.2(t)	104.5(t)	100.3(t)	3.9	4.2
9	29.6(q)	29.2(q)	29.9(q)	−0.3	−0.7
10	25.7(q)	25.4(q)	26.2(q)	−0.5	−0.8

a) The spectra were measured in $CDCl_3$ with an internal standard of TMS. Multiplicities given in parentheses were determined by off-resonance ^{1}H decoupled spectra. b) For the additional $-COCH_3$ 170.6(s) and 21.4(q) were given. c) The assignment depended upon Ref. 14. d) Effects of hydroxy or acetoxy group are reported at designated position relative to camphene (**7**).

alcohol gave an oily monoacetate, $C_{12}H_{18}O_2$ (M^+ 194); ν 1740 and 1250 cm^{-1}, which was identical with the co-occurring acetate in IR, ^{1}H-NMR, and MS spectra. The reduction of the co-occurring acetate with $LiAlH_4$ afforded an alcohol showing the same TLC behavior as nojigiku alcohol.

With regard to the ^{13}C-NMR spectra of nojigiku alcohol and its acetate the shielding differences of the carbon atoms ($\Delta\delta$ in Table 1) were calculated for those of camphene. In this case the differences showed the same trend as in the case of 5-*exo*-hydroxynorbornane towards norbornane.[8)] In the ^{1}H-NMR spectra of the alcohol, its acetate, and dihydro alcohol the carbinyl protons uniformly showed a double doublet (J=7.0 and 3.0 Hz) at δ 3.71, 4.55, and 3.97, which indicated the protons on C-5 to have the *endo* configuration.[9)] Furthermore, the cyclopentanone derivative (**3**) was reduced with $LiAlH_4$ to give two epimeric alcohols in a ratio of 9: 1. Of these products the minor alcohol was identical with nojigiku alcohol in IR, ^{1}H-NMR, and MS spectra. The major alcohol could be characterized as its epimer (**6**) holding the hydroxyl group in the *endo* configuration based on the fact that a broad doublet (δ 2.67) of the allylic bridgehead proton had a coupling constant of about J=4.0 Hz as well as that of (J=3.8 Hz) in *endo*-norborneol.[9)] These facts clearly designated the hydroxyl group of nojigiku alcohol to have the *exo* configuration. The proposed structure for nojigiku alcohol, however, has been reported to a chlorination product of camphene by some workers.[10a—d)] For confirmation of the identity, the compound was synthesized from *dl*-camphene according to the reports;[10b,d)] the IR, ^{1}H-NMR, and MS spectra were respectively coincident with those of nojigiku alcohol.

In order to determine the absolute configuration of nojigiku alcohol, its dihydro alcohol (**4**) was oxidized with Jones reagent to a saturated ketone (**5**) which showed a negative Cotton effect ($[\phi]_{297}$ −4690, $[\phi]_{265}$ +1600, c 0.039, MeOH) on the ORD curve. This indicated, according to the relation between the Cotton effect and stereostructure in a bicyclo[2.2.1]heptan-2-one system,[11)] that the saturated ketone had an absolute configuration as shown by (**5**). Consequently, the absolute configuration of nojigiku alcohol and its acetate isolated from *Ch. japonense* may be represented as formulae (**1**) and (**2**) holding the chirality of *d*-camphene. The configuration of the hydroxyl group in this formula (**1**) agreed with the determination by Horeau's method.[12)]

Other Constituents of the Essential Oil. From the essential oil of *Ch. japonense* fifteen monoterpenoids and nine sesquiterpenoids were identified other than nojigiku alcohol and its acetate as shown in Table 2. The composition, calculated from the relative GLC peak areas and identification methods are also listed. Total amounts of the monoterpenoids and sesquiterpenoids were *ca.* 87 and 13%, respectively, in the oil. The monoterpenoids thus identified have been classified into the camphane type ((+)-camphene, (+)-camphor, nojigiku alcohol and its acetate, (+)-borneol, and (+)-bornyl acetate), the pinane type ((+)-α-pinene, β-pinene, (+)-chrysanthenone, (+)-*trans*- and (−)-*cis*-chrysanthenyl acetate), *p*-menthane type (1,8-cineole, *p*-cymene, *trans*- and *cis*-carveyl acetate), and others (sabinene and filifolone). The camphane, pinane and *p*-menthane types were respectively 74.8, 6.5, and 5.5% of the total oil. Thus, the major part of the oil consisted of bicyclic monoterpenoids, in which (+)-camphor was the main (60.0%), and the other monoterpenoids were in trace amounts except for 1,8-cineole. As to the pinane type, (+)-*trans*-chrysanthenyl acetate has been previously isolated from the essential oil of *Ch. shiwogiku*[3)] by the present author *et al.*, and (−)-*cis*-chrysanthenyl acetate has been reported as the main component of *Centipeda Cunninghami*[13)] by Pinhey and Southwell. Both isomers, however, co-occurred in this essential oil. (+)-Chrysanthenone, (+)-*trans*- and (−)-*cis*-chrysanthenyl acetate should be counted in the series of (−)-α-pinene in the chirality, but any oxygenated derivative of (+)-α-pinene could not be identified in the oil.

The essential oil of *Ch. japonense* remarkably differed from that of *Ch. japonense var. devile*,[6)] which contains borneol and bornyl acetate as major components but not nojigiku alcohol and its acetate, although the latter has been classified as a variety of the former.

Table 2. Constituents of the essential oil of *Ch. japonense*

	Compound	Content (% in total oil)		Method of identification
Monoterpenoids				
Camphane type	(+)-Camphene	2.3	74.8	IR, NMR, MS
	(+)-Camphor	60.0		IR, NMR, MS
	(+)-Nojigiku alcohol	5.4		IR, NMR, MS
	(+)-Borneol	1.5		IR, NMR, MS
	(+)-Bornyl acetate	4.3		IR, NMR, MS
	(+)-Acetate of nojigiku alcohol	1.3		IR, NMR, MS
Pinane type	(+)-α-Pinene	1.4	6.5	IR, MS
	β-Pinene	0.6		IR, MS
	(+)-Chrysanthenone	2.4		IR, NMR, MS
	(+)-*trans*-Chrysanthenyl acetate	1.3		IR, NMR, MS
	(−)-*cis*-Chrysanthenyl acetate	0.8		IR, NMR, MS
p-Menthane type	1,8-Cineole	4.8	5.5	IR, NMR, MS
	p-Cymene	0.4		IR, MS
	trans-Carveyl acetate	0.2		IR, NMR, MS
	cis-Carveyl acetate	0.1		IR, NMR, MS
Other	Sabinene	0.2	0.6	IR, MS
	Filifolone	0.4		IR, NMR, MS
Sesquiterpenoids				
Hydrocarbons	α-Copaene	0.1	9.6	IR, NMR, MS
	β-Elemene	1.0		IR, NMR, MS
	β-Caryophyllene	1.2		IR, NMR, MS
	Germacrene-D	6.7		IR, NMR, MS
	γ-Cadinene	0.3		IR, NMR, MS
	Calamenene	0.2		IR, MS
Oxygenated compounds	β-Caryophyllene oxide	1.1	3.5	IR, NMR, MS
	T-Muurolol	1.6		IR,15) NMR, MS
	α-Cadinol	0.1		IR,15) NMR, MS
	Unidentified	0.7		

Experimental

All melting and boiling points are uncorrected. The IR spectra were measured in CCl_4. The ^{1}H-NMR spectra were obtained on a Hitachi R-20 or Varian T-60 spectrometer in CCl_4 using TMS as the internal standard. The ^{13}C-NMR spectra were recorded on a JEOL-PFT-100 spectrometer operating at 25.5 MHz. The mass spectra were measured on a Hitachi RMS-4 spectrometer, and the high mass measurements on a Hitachi RMU-7L spectrometer. The TLC was carried out using a Merck Kiesel Gel G, and the elution chromatography using a Merck Kiesel Gel Type 60. The analytical GLC was performed with a separation column (3 mm×2 m) packed with 3% PEG-6000, PEG-20M, DEGS, and SE-30 on Chromosorb AW (60—80 mesh) under the flow rate of 20 ml/min of N_2, and preparative GLC with a separation column (6 mm×2 m) packed with 10% PEG-6000, PEG-20M, DEGS, and SE-30 on Chromosorb AW (60—80 mesh) using He as a carrier gas (30 ml/min).

Separation and Fractionation of the Essential Oil[1] *Ch. japonense* used in the experiment was collected at the sea side of Suzaki city in Kochi prefecture in October prior to efflorescence. After being dried in the shade for one day, the plant (8.1 kg) was steam distilled to obtain the essential oil (6.0 g, yield 0.07%), $[\alpha]^{25}_{\rm D}$ −1.86°, $n^{25}_{\rm D}$ 1.4800, d^{25}_{4} 0.9388, including an ether extract from the distilled water. The essential oil showed twenty six GLC peaks using a SE-30 column under a temperature programme of 3 °C/min from 80 to 200 °C.

The oil was fractionated through a small size-spinning band distillation column (6×500 mm) under reduced pressure and separated into the following fractions and residue (2.4 g). Fr. 1 (bp 40—60 °C/30 Torr): 1.2 g; fr. 2 (60—80 °C/20 Torr): 1.0 g; fr. 3 (80—100 °C/20 Torr): 0.9 g. The residue was then eluted stepwise over a silica gel column by hexane (100 ml), a hexane and ethyl acetate mixture (v/v, 3: 1, 200 ml), and diethyl ether (100 ml) to give three additional fractions, R-1, R-2, and R-3, respectively.

Isolation of Nojigiku Alcohol (1) and Its Acetate (2). Fraction R-2 was again eluted over a silica gel column with a mixed solvent of hexane and ethyl acetate (v/v, 5: 1) and nojigiku alcohol isolated from the last eluate in a homogeneous state for GLC (SE-30 and PEG-20M). MS *m/e* 152 (M^+, $C_{10}H_{16}O$, 0.5%), 137 ($M-CH_3$, 3%), 135 (M−OH, 4%), 134 ($M-H_2O$, 3%), 108 (base), 119 (14), 93 (62), 91 (39), 81 (13), 79 (29), 67 (21), and 41 (34). 3,5-Dinitrobenzoate, Found: C, 58.97; H, 5.23; N, 8.06%. Calcd for $C_{17}H_{18}N_2O_6$: C, 58.95; H, 5.24; N, 8.09%.

Acetylation of the alcohol (30 mg) with Ac_2O (1 ml) in pyridine (1 ml) gave an oily monoacetate (35 mg). $[\alpha]^{25}_{\rm D}$ +11.6° (*c* 1.20, $CHCl_3$). The IR, ^{1}H-NMR, and MS spectra were respectively superimposable on those of the co-occurring acetate described in the following.

The early eluate in the column chromatography of fraction R-2 afforded an oily mixture of monoterpene acetates showing six GLC peaks, the fourth peak of which was characterized, after isolation by preparative GLC (PEG-20M, 110 °C), as the acetate (**2**) of nojigiku alcohol based on the following data.

MS *m/e* 194.1309 (M$^+$, 1.9%, calcd for $C_{12}H_{18}O_2$, 194.1312), 179 (3), 150 (35), 134 (4), 119 (12), 107 (58), 93 (13), 91 (13), 89 (17), 79 (11), 77 (7), 67 (8), 65 (5), 53 (8), 43 (base), and 41 (18); IR ν 3075, 1740, 1655, 1375, 1365, 1250, 1035, and 895 cm^{-1}; ^{1}H-NMR δ 1.07 (6H, s), 1.95 (3H, s), 2.73 (1H, br s), 4.55 (1H, dd, *J*=7.0 and 3.0 Hz), 4.73 (1H, s), and 4.99 (1H, s). Found: C, 74.35; H, 9.41%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

The acetate was applied to the TLC plate, and some drops of an ethereal solution of $LiAlH_4$ applied. After standing for a times, the plate was developed with $CHCl_3$ and a mixture of hexane and ethyl acetate (v/v, 5: 1), giving an R_f 0.30 or 0.35. This mobility agreed with that of nojigiku alcohol.

Catalytic Hydrogenation of Nojigiku Alcohol. The alcohol (70 mg) was subjected to hydrogenation over Adams catalyst (5 mg) in AcOH (3 ml) at room temperature until the uptake of H_2 ceased. The hydrogenated mixture was treated in the usual manner to give a product showing two peaks attributable to two diastereoisomers of dihydronojigiku alcohol in GLC (DEGS) with a relative peak intensity of about 4: 1. The major product was isolated by preparative GLC (DEGS) to give the 3-*endo*-methyl isomer (**4**) as colorless needles, mp 68.0—69.0 °C. MS *m/e* 154 (M$^+$, $C_{10}H_{18}O$, 3%), 139 (5), 121 (6), 110 (6), 95 (29), 84 (14), 81 (12), 71 (22), 67 (30), 55 (47), and 41 (base); IR ν 3620, 3320, 1390, 1375, 1365, and 1040 cm^{-1}; ^{1}H-NMR δ 0.75 (3H, s), 0.87 (3H, s), 0.90 (3H, d, *J*=6.0 Hz), 1.70 (1H, br s, OH exchanged with D_2O), and 3.97 (1H, dd, *J*=7.0 and 3.0 Hz).

*Oxidation of 3-*endo*-Methyl Alcohol (4).* The 3-*endo*-methyl alcohol (45 mg) was oxidized with Jones reagent (1 ml) in acetone (5 ml) at room temperature. After the usual work up, the mixture gave a crystalline ketone (**5**) (30 mg), mp 58.0—59.0 °C. MS *m/e* 152 (M$^+$, 21%), 137 (10), 123 (4), 119 (12), 117 (14), 110 (34), 95 (96), 83 (20), 81 (29), 69 (41), 67 (32), 55 (59), and 41 (base); IR ν 1750, 1420, 1390, 1380, and 1365 cm^{-1}; ^{1}H-NMR δ 0.83 (3H, d, *J*=6.0 Hz), 0.92 (3H, s), 1.17 (3H, s), and 2.35 (1H, br d, *J*=4.0 Hz).

Oxidation of Nojigiku Alcohol (1). To the alcohol (120 mg) in acetone (10 ml) Jones reagent (2 ml) was added drop by drop at room temperature. After the brown color of the reaction mixture disappeared, it was treated according to the usual procedure and purified over a silica gel column with $CHCl_3$ to give an unsaturated ketone (**3**) as a colorless solid. $[\alpha]_D^{25}$ +33.7° (*c* 0.86, $CHCl_3$). MS *m/e* 150.1049 (M$^+$, 27%, calcd for $C_{10}H_{14}O$, 150.1044), 135 (17), 121 (11), 107 (81), 106 (86), 91 (77), 79 (69), 77 (41), 67 (25), 65 (24), 53 (44), and 41 (base); IR ν 3075, 1755, 1665, 1420, 1390, 1370, 1150, and 899 cm^{-1}; ^{1}H-NMR δ 1.13 (3H, s), 1.22 (3H, s), 3.00 (1H, br s), 4.82 (1H, s), and 5.06 (1H, s).

Reduction of the Unsaturated Ketone (3). To a suspention of $LiAlH_4$ (20 mg) in dry diethyl ether (5 ml) an ethereal solution of the ketone (**3**) (75 mg/2 ml) was added drop by drop and the mixture stirred at room temperature for 3 h. After the excess reagent was decomposed by adding H_2O (1 ml), the ethereal layer was separated, washed with 1% H_2SO_4 and H_2O, dried over Na_2SO_4 and concentrated to give a colorless oil (69 mg). GLC (DEGS) showed two peaks with an intensity ratio of 9: 1, which were eluted over a silica gel column with $CHCl_3$. The major compound thus obtained gave an R_f 0.37 in TLC using $CHCl_3$ as a solvent and it was thus characterized as the *endo*-hydroxy isomer (**6**) of nojigiku alcohol. mp 67.5—68.5 °C. MS *m/e* 152.1189 (M$^+$, 1%, calcd for $C_{10}H_{16}O$, 152.1200), 137 (4), 135 (3), 134 (2), 119 (14), 108 (87), 93 (54), 91 (34), 81 (15), 79 (20), 77 (32), 67 (35), 65 (22), 55 (34), 53 (44), 51 (22), 43 (30), and 41 (base); IR ν 3540, 3075, 1660, 1398, 1380, 1125, 1045, and 895 cm^{-1}; ^{1}H-NMR δ 1.12 (6H, s), 2.68 (1H, br d, *J*=4.0 Hz), 4.03 (1H, m), and 4.93 (2H, s). 3,5-Dinitrobenzoate, mp 136.5—138.0 °C.

The minor compound gave R_f 0.30 in TLC which was identical with nojigiku alcohol in IR, ^{1}H-NMR, and MS spectra.

Absolute Configuration of the Hydroxyl Group in Nojigiku Alcohol by Horeau's Method.[12] α-Phenylbutylic anhydride was prepared by refluxing racemic α-phenylbutylic acid with acetic anhydride for 5 h and evaporation of the solvent *in vacuo*. The racemic anhydride (1.2 mmol) was added to a solution of the alcohol (0.4 mmol) in pyridine (2 ml), and the mixture allowed to stand for 20 h at room temperature. After the excess anhydride was decomposed with H_2O (1.0 ml), the mixture was diluted with benzene and titrated with 0.1 M NaOH using phenolphthalein as indicator. The aqueous layer was separated, acidified with 0.5 M H_2SO_4 and extracted with benzene. The benzene solution was dried and evaporated under reduced pressure to give an oily α-phenylbutylic acid. The acid thus recovered was dissolved in benzene (5 ml), and the optical rotation measured in a 0.5 dm cell as $[\alpha]_D^{25}$ +10.0°. Thus the optical yield was calculated as +56.3%.

Synthesis of Nogigiku Alcohol. Camphene (1.0 g) was sealed in a pyrex tube with *t*-butyl hypochlorite (1.2 g) and irradiated with a tungsten lamp (40 W) for 9 h in an ice bath.[10b] The mixture was fractionated under reduced pressure (70 °C/1 Torr) to give a distillate, which separated by preparative GLC (PEG-20M, 125 °C) to afford *exo*-6-chlorocamphene. MS *m/e* 172 and 170 (7 and 19%, M$^+$ for $C_{10}H_{15}Cl$), 157 (9), 155 (24), 135 (37), 121 (30), 119 (27), 107 (50), 93 (base), 91 (50), 79 (40), 77 (47), 67 (27), 53 (20), and 41 (45); IR ν 3060, 1660, 1385, 1360, 1300, 1095, 890, and 770 cm^{-1}; ^{1}H-NMR δ 0.98 (3H, s), 1.06 (3H, s), 2.81 (1H, br s), 3.80 (1H, dd, *J*=7.0 and 3.5 Hz), 4.68 (1H, s), and 4.93 (1H, s).

The chlorocamphene (120 mg) was then refluxed[10d] with Li_2CO_3 (60 mg) in water for 10 h. The resulting alcohol was extracted with ether, and purified by preparative GLC (PEG-20M, 125 °C). The compound thus synthesized was identical with nojigiku alcohol in IR, ^{1}H-NMR, and MS spectra.

Identification of Other Monoterpenoids in the Essential Oil. Fraction 1 and 2, which were separated by fractional distillation from the oil, were further treated by preparative GLC (PEG-6000, 80 °C) to isolate six hydrocarbons which were identified on the spectra listed in Table 2. Among them, (+)-α-pinene: $[\alpha]_D^{25}$ +17.1° (*c* 0.80, $CHCl_3$), (+)-camphene: $[\alpha]_D^{25}$ +82.7° (*c* 1.60, $CHCl_3$).

Fraction R-2, which was separated from the fractional distillation residue of the oil by elution chromatography, was again chromatographed over silica gel with hexane and ethyl acetate (v/v, 5: 1). The first eluate was treated with preparative GLC (SE-30, 120 °C and PEG-20M, 110 °C) to give six monoterpene acetates including the acetate of nojigiku alcohol, identified as shown in Table 2. From the middle eluate, three ketones and an alcohol were isolated by a combination of additional chromatography (hexane and ethyl acetate, v/v, 5: 1) and preparative GLC (PEG-20M, 120 °C). Spectral data of these compounds were as follows.

(+)-trans-*Chrysanthenyl Acetate*: $[\alpha]_D^{25}$ +36.7° (*c* 1.40, $CHCl_3$); MS *m/e* 194 (M$^+$, 1.5%), 179 (1), 151 (5), 137(8), 135 (29), 119 (24), 93 (17), 91 (28), 81 (23), 69 (10), 67 (12), 59 (14), and 43 (base); IR ν 3025, 1740, 1375, 1360, 1250, 1180, 1033, and 791 cm^{-1}; ^{1}H-NMR δ 0.89 (3H, s), 1.25 (3H, s), 1.57 (3H, q, *J*=2.0 Hz), 1.88 (3H, s), 4.87 (1H, t, *J*=6.0 Hz), and 5.30 (1H, m).

(−)-cis-*Chrysanthenyl Acetate*: $[\alpha]_D^{25}$ −25.5° (*c* 1.10, $CHCl_3$); MS *m/e* 194 (M$^+$, 1%), 179 (2), 137 (9), 135 (26), 119 (61), 109 (27), 91 (26), 81 (25), 69 (15), 67 (14), 59 (21), 43 (base) and 41 (37); IR ν 3030, 1740, 1375, 1360, 1240, 1040, and 720 cm^{-1}; ^{1}H-NMR δ 0.91 (3H, s), 1.43 (3H, s), 1.70 (3H, q, J=2.0 Hz), 2.01 (3H, s), 4.45 (1H, s), and 5.23 (1H, m) (IR and ^{1}H-NMR values in agreement with authentic spectra provided by professor J. T. Pinhey, University of Sydney).

trans-*Carveyl Acetate*: ^{1}H-NMR δ 1.67 (3H, m), 1.70 (3H, br s), 1.97 (3H, s), 4.70 (2H, m), 5.18 (1H, m), and 5.65 (1H, br d, J=6.0 Hz).

cis-*Carveyl Acetate*: ^{1}H-NMR δ 1.64 (3H, m), 1.74 (3H, br s), 2.00 (3H, s), 4.73 (2H, br s), and 5.30 (1H, m).

(+)-*Bornyl Acetate*: $[\alpha]_D^{25}$ +20.7° (c 5.70, $CHCl_3$)

Filifolone: MS m/e 150 (M$^+$, 30%), 135 (14), 122 (35), 107 (base), 93 (35), 91 (65), 85 (43), 80 (83), 79 (63), 70 (61), 57 (43), 55 (32), 43 (48), and 41 (72); IR ν 1779 cm^{-1}; ^{1}H-NMR δ 1.08 (3H, s), 1.17 (3H, s), 1.75 (3H, br s), 2.53 (3H, m), 4.00 (1H, m), and 5.35 (1H, m) (IR and ^{1}H-NMR spectra in agreement with authentic ones provided by Professor R. B. Bates, University of Arizona).

(+)-*Chrysanthenone*: $[\alpha]_D^{25}$ +61.0° (c 1.50, $CHCl_3$); MS m/e 150 (M$^+$, 1.7%), 135 (7), 122 (20), 107 (base), 91 (57), 79 (30), 69 (17), 55 (12), 53 (14), 43 (10), and 41 (32), IR ν 1780 cm^{-1}; ^{1}H-NMR δ 1.18 (3H, s), 1.20 (3H, s), 1.70 (3H, q, J=2.0 Hz), 2.51 (2H, m), and 5.30 (1H, m).

(+)-*Camphor*: Mp 178 °C; $[\alpha]_D^{25}$ +25.4° (c 3.10, $CHCl_3$). Oxime: Mp 118.0—118.5 °C. Semicarbazone: Mp 236.0—237.0 °C.

(+)-*Borneol*: Mp 204.0—205.0 °C; $[\alpha]_D^{25}$ +10.8° (c 1.80, EtOH). 3,5-Dinitrobenzoate: mp 155.5—156.0 °C.

Identification of Sesquiterpenoids in the Essential Oil. The hexane eluate in the chromatography of fr. R-2 was further treated by preparative GLC (PEG-20M, 150 °C) to give six sesquiterpene hydrocarbons. Fr. R-3 was also treated in combination of silica gel column chromatography (petroleum ether and diethyl ether, v/v, 3: 1) and preparative GLC (SE-30, 200 °C) to give three oxygenated sesquiterpenes. These compounds thus isolated, were identified on the basis of the IR, ^{1}H-NMR, and MS spectra, are listed in Table 2.

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